Contents

Foreward xi
Preface xv

HISTORY OF THE f-ELEMENTS

Invited lectures:

Lanthanides since 1839: from crowded elements to quantum-chemical Rosetta Stone 1
C. K. Jørgensen (Geneva, Switzerland)

Concepts and techniques in the discovery of the actinide elements 7
A. G. Maddock (Cambridge, U.K.)

I. COORDINATION CHEMISTRY

Invited lectures:

Some aspects of the coordination and organometallic chemistry of thorium and uranium (M^{III}, M^{IV}, U^{V}) in +3 and +4 oxidation states 13
P. C. Blake, M. F. Lappert, R. G. Taylor (Brighton, U.K.), J. L. Atwood and Hongming Zhang (Alabama, Ala., U.S.A.)

New trends in the structural chemistry of actinide and lanthanide coordination compounds . 21
G. Bombieri (Milan, Italy)

Europium(III) complexation reactions in water. 33
H. B. Silber (San Jose, Calif., U.S.A.)

Schiff base complexes of lanthanides and actinides 39
P. A. Vigato (Padua, Italy) and D. E. Fenton (Sheffield, U.K.)

Posters:

Crystal structures of three UO_2^{2+} complexes with S-donors 49
M. Pennington, N. W. Alcock (Coventry, U.K.) and D. Brown (Didcot, U.K.)

Crystal structure of the adduct of thorium(IV) tetrakisacetylacetonate with aniline $[Th(C_5H_7O_2)_4]_2 \cdot C_6H_5NH_2$. 51
P. J. Reeves and A. J. Smith (Sheffield, U.K.)

A novel (3 + 3) hexaimine Schiff base macrocyclic complex of lanthanum 55
D. E. Fenton, S. J. Kitchen, C. M. Spencer (Sheffield, U.K.), P. A. Vigato and S. Tamburini (Padua, Italy)

Lanthanide complexes with macrocyclic and macroacyclic Schiff bases 59
E. Bullita, U. Casellato, P. Guerriero and P. A. Vigato (Padua, Italy)

Actinide complexes with Schiff bases: the first crystal structure of a binuclear thorium(IV) complex with a pentadentate compartmental ligand. 61
U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato and R. Graziani (Padua, Italy)

Dioxouranium(VI) complexes with polydentate Schiff bases containing acetal groups 65
S. Sitran, D. Fregona, U. Casellato, P. A. Vigato and G. Faraglia (Padua, Italy)

Lanthanide complexes with pyridine-2,6-dicarboxylic and thiophene-2,5-dicarboxylic acids . 67
P. Guerriero, U. Casellato, S. Sitran, P. A. Vigato and R. Graziani (Padua, Italy)

Novel Schiff base complexes of some f-transition and related elements 69
H. A. Tayim (Riyadh, Saudi Arabia)

© Elsevier Sequoia/Printed in Switzerland

Polypyrazolylborate complexes of yttrium and lanthanum 71
D. L. Reger, J. A. Lindeman and L. Lebioda (Columbia, S.C., U.S.A.)

Mixed pyrazolylborate–β-diketonate–Ln(III) complexes 75
W. D. Moffat, M. V. R. Stainer and J. Takats (Edmonton, Alta., Canada)

Synthesis and characterization of $UCl_2[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pz)$ and $MCl_3[HB(3,5\text{-}Me_2pz)_3](3,5\text{-}Me_2pzH)$ (M = U(IV) and Th(IV); pz = pyrazolyl). 79
N. Marques, J. Marçalo, A. Pires de Matos (Sacavém, Portugal), K. W. Bagnall (Manchester, U.K.) and J. Takats (Edmonton, Alta., Canada)

U(IV) and Th(IV) hydrotris(3,5-dimethylpyrazolyl)borate complexes with asymmetric metal centres 83
N. Marques, J. Marçalo, T. Almeida, J. M. Carretas, A. Pires de Matos (Sacavém, Portugal), K. W. Bagnall (Manchester, U.K.) and J. Takats (Edmonton, Alta., Canada)

Reduction of uranium(IV) complexes containing the hydrotris(3,5-dimethylpyrazolyl)borate ligand 87
Uranium(IV) bishydrotris(pyrazol-1-yl)boratothiolato derivatives. 89
I. Santos, N. Marques and A. Pires de Matos (Sacavém, Portugal)

Preparation and crystal structures of tetrakis(methyltrihydroborato)uranium(IV)bis(tetrahydrofuranate) and tetrakis(methyltrihydroborato)uranium(IV)tetrahydrothiophenate 91
Preparation of some Lewis base adducts of tris(methyltrihydroborato)Ho and Yb and crystal structures of tris(methyltrihydroborato)ytterbium(III)etherate and tris(methyltrihydroborato)holmium(III)bis(pyridine) 97
R. Shinomoto, A. Zalkin and N. M. Edelstein (Berkeley, Calif., U.S.A.)

Crystal structure of a dysprosium trichloride complex with oxygen donor ligands 103
Zhang Xing-wang, Li Xing-fu (Beijing, China), F. Benetollo (Padua, Italy) and G. Bombieri (Milan, Italy)

Recent advances in the chemistry of UX_4 complexes (X = Cl, Br and I) 105
J. G. H. du Preez and B. Zeelie (Port Elizabeth, South Africa)

Ultrasonic relaxation measurements on erbium chloride in water and aqueous methanol 107
H. B. Silber and Yue Zhang (San Jose, Calif., U.S.A.)

Possible stabilization of the tetravalent oxidation state of berkelium and californium in acetonitrile with triphenylarsine oxide. 111
G. F. Payne and J. R. Peterson (Oak Ridge, Tenn., U.S.A.)

A Mössbauer effect study of some europium(III) nitrate complexes with unidentate oxygen-donor ligands 113
F. Grandjean (Sart-Tilman, Belgium), G. J. Long, M. L. Buhl (Rolla, Mo., U.S.A.), U. Russo, B. Zarli and G. Valle (Padua, Italy)

Thermodynamics of Ln(III) complexation with AMP and ATP. 119
S. M. Shanbhag and G. R. Choppin (Tallahassee, Fla., U.S.A.)

Studies on lanthanoid sulfites.
Part VII. Preparative and thermal study on rare earth sulfite sulfate hydrates 121
M. Leskelä, J. Everardo X. de Matos and L. Niinistö (Espoo, Finland)

Thermal decomposition of octakis(*p*-dimethylphenylsulfoxide)lanthanide(III) perchlorates in a helium atmosphere. 125
M. A. Bañares, M. E. Pérez and R. J. Ruano (Salamanca, Spain)

Synthesis and characterization of sodium di-μ-hydroxo-bis[3,6-disulpho-1,2-naphthoquinone-1-oximato-*O,N*-dioxouranate(VI)] 129
A. Vainiotalo, T.-P. Jauhiainen, J. Vepsäläinen and M. Kauppinen (Joensuu, Finland)

Synthesis and crystal structure of a complex [perrhenate-bis(1,4-dithiane 1,4-dioxide)mono-(μ-1,4-dithiane 1,4-dioxide)triaquaholmium(III) polymer] perrhenate-1,4-dithiane 1,4-dioxide 131
J. M. Miranda, M. A. Oliveira, E. E. Castellano (São Carlos, Brazil), E. Scoralick, L. B. Zinner and G. Vicentini (São Paulo, Brazil)

Synthesis and characterization of several lanthanide complexes with ethyl α-ketocyclopentyl carboxylate 135
M. A. Bañares, A. Angoso, J. L. Manzano, E. Rodríguez and M. T. Blasco (Salamanca, Spain)

^{31}P and ^{23}Na NMR lanthanide induced shifts in axially symmetric macrocyclic phosphonate complexes 137
A. D. Sherry, C. F. G. C. Geraldes and W. P. Cacheris (Richardson, Tex., U.S.A.)

Studies on the kinetics of formation and dissociation of the cerium(III)–DOTA complex . . . 141
E. Brücher, G. Laurenczy and Zs. Makra (Debrecen, Hungary)

The formation of mixed complexes of NdMEDTA and NdHyEDTA with acetate. 143
W. D'Olieslager, M. De Jonghe, M. Wevers and L. Heerman (Heverlee, Belgium)

Water exchange kinetics on lanthanide(III) ions: a variable temperature and pressure ^{17}O NMR study 147
C. Cossy, L. Helm and A. E. Merbach (Lausanne, Switzerland)

^{139}La NMR and quantitative FT-IR investigation of the interaction between Ln(III) ions and various anions in organic solvents 151
J.-C. G. Bünzli, A. E. Merbach and R. M. Nielson (Lausanne, Switzerland)

Competitive equilibria in lanthanide trifluoromethanesulfonate solutions in propylene carbonate containing a 15-crown-5 ether 153
F. Pilloud and J.-C. G. Bünzli (Lausanne, Switzerland)

Synthesis and characterization of complexes of neodymium(III) with piperazines 155
Arun Kumar Trikha (Patiala, India)

Dioxouranium(VI) complexes with γ-disulfoxides 159
E. B. de Paiva e Sá, M. I. D. Holanda and J. A. P. Holanda (Fortaleza-Ceará, Brazil)

Synthesis and infrared studies of dichlorolanthanide complexes of ethyl 2-(diphenyloxophosphino)acetates 161
Hsu-kun Wang, Ming-jie Zhang and Ji-tao Wang (Tianjin, China)

Complexation of trivalent lanthanides and yttrium by benzylidenepyruvates in aqueous solution 163
C. B. Melios, J. T. Souza Campos, M. A. C. Mazzeu, L. L. Campos, M. Molina and J. O. Tognolli (Araraquara, Brazil)

Synthesis and characterization of rare earth monophthalocyanine complexes 165
Ni Jiazan, Shi Feng, Li Zhenxiang and Yin Shaoming (Changchun, China)

II. ORGANOMETALLIC CHEMISTRY

Invited Lectures:

Synthesis, structure and reactivity of organometallic complexes of Sm(II) 169
W. J. Evans (Irvine, Calif., U.S.A.)

Reactivity of the uranium–carbon σ-bond in 'silylamido' compounds 171
A. Dormond, A. Aaliti, A. El Bouadili and C. Moise (Dijon, France)

Small molecule activation at the uranium carbon multiple bond 177
J. W. Gilje and R. E. Cramer (Honolulu, Hawaii, U.S.A.)

Posters:

Tris(2,6-di-t-butylphenoxo)yttrium: a three-coordinate hydrocarbon-soluble aryloxide of yttrium 183
P. B. Hitchcock, M. F. Lappert and R. G. Smith (Brighton, U.K.)

The synthesis and X-ray structure of a novel monocyclopentadienyluranium(IV) chloride $[UCp'''Cl_2(THF)(\mu\text{-}Cl)_2Li(THF)_2]$ [$Cp''' = \eta\text{–}C_5H_2(SiMe_3)_3$-1,2,4] 185
M. A. Edelman, M. F. Lappert (Brighton, U.K.), J. L. Atwood and Hongming Zhang (Alabama, Ala., U.S.A.)

Organoactinide complexes.
Part I. Synthesis and structure of tris(cyclopentadienyl)uranium fluoroalkoxides. 187
F. Knösel, H. W. Roesky and F. Edelmann (Göttingen, F.R.G.)

The reaction of diiodoethane with neptunium and plutonium metals. 189
D. G. Karraker (Aiken, S.C., U.S.A.)

Reduced biuranocenylene – a mixed valence organouranium compound? 193
A. Streitwieser, Jr. and D. C. Eisenberg (Berkeley, Calif., U.S.A.)

Studies on organolanthanide complexes.
XVII. Syntheses and identification of 1,1′-pentamethylenedicyclopentadienyl lanthanide chlorides, yttrium chloride and yttrium cyclopentadienyl derivative 195
Changtao Qian, Zuowei Xie and Yaozeng Huang (Shanghai, China)

The coordination chemistry of trivalent uranium and cerium 201
J. G. Brennan, S. D. Stults, R. A. Andersen and A. Zalkin (Berkeley, Calif., U.S.A.)

Studies on rare earth allyl compounds.
IV. The crystal structure of $[Li_2(\mu\text{-}C_3H_5)(C_4H_8O_2)_3][Ce(\eta^3\text{-}C_3H_5)_4]$ 203
Zuen Huang, Mingqin Chen, Wenjie Qiu and Wenling Wu (Shanghai, China)

Crystal and molecular structure of a novel organoactinide complex: $[U(C_5H_5)_3(NCCH_3)_2]^+$-$[Th(C_5H_5)Cl_4(NCCH_3)]^-$ 209
J. Rebizant, C. Apostolidis (Karlsruhe, F.R.G.), M. R. Spirlet (Liège, Belgium) and B. Kanellakopulos (Karlsruhe, F.R.G.)

Structural investigations of the isomorphous propionitrile-tris(η^5-cyclopentadienyl) lanthanoid(III) (Ln = La, Pr, Yb) complexes and of the corresponding 1:2 adducts 211
M. R. Spirlet (Liège, Belgium), J. Rebizant, C. Apostolidis and B. Kanellakopulos (Karlsruhe, F.R.G.)

Structural chemistry of lanthanide dicyclopentadienide halides.
Part 5. Gadoliniumdicyclopentadienidechloride $[Gd(C_5H_5)_2Cl]_4$ 215
W. Lamberts, B. Hessner and H. Lueken (Aachen, F.R.G.)

III. THEORY AND SPECTROSCOPY

Invited Lectures:

The europium(III) ion as spectroscopic probe in bioinorganic chemistry 219
J.-C. G. Bünzli (Lausanne, Switzerland)

Spectroscopic properties of tetravalent actinide ions in solids. 223
J. C. Krupa (Orsay, France)

Recent developments in the theory of f-element molecules 243
P. Pyykkö (Helsinki, Finland)

An MO study on structures and reactivity of organoactinides based on the extended Hückel method: actinide bis(cyclopentadienyl) complexes 247
K. Tatsumi and A. Nakamura (Osaka, Japan)

Posters:

Crystal field effects in lutetium disilicates doped with Eu^{3+} 253
J. Hölsä, P. Porcher (Espoo, Finland) and C. Chateau (Meudon, France)

Luminescence of Eu^{3+} ion as a structural probe in high temperature phase transformations in lutetium orthoborates 257
J. Hölsä (Espoo, Finland)

Photoluminescence study of Tb^{3+} doped alkaline earth sulfide thin films 261
M. Asplund, J. Hölsä, M. Leskelä, L. Niinistö and E. Nykänen (Espoo, Finland)

Energy transfer in some luminescent gadolinium fluorides 265
R. Mahiou, J. Metin, D. Zambon, A. Arbus, M. T. Fournier and J. C. Cousseins (Aubière, France)

Optical properties of U^{4+} in α-$ThBr_4$ 269
E. Simoni, S. Hubert and M. Genet (Orsay, France)

Laser induced fluorescence of $^{249}Bk^{4+}$ in CeF_4 273
G. M. Jursich, J. V. Beitz, W. T. Carnall, G. L. Goodman, C. W. Williams and L. R. Morss (Argonne, Ill., U.S.A.)

Crystal-field analysis of Tb^{3+}:LaF_3 and Gd^{3+}:LaF_3 in C_{2v} site symmetry 275
W. T. Carnall, G. L. Goodman, G. M. Jursich (Argonne, Ill., U.S.A.), R. S. Rana (Worcester, Mass., U.S.A.), P. Vandevelde, L. Fluyt and C. Görller-Walrand (Heverlee, Belgium)

A spectroscopic study of the $TbAl_3(BO_3)_4$ crystal 277
C. Görller-Walrand, P. Vandevelde, I. Hendrickx (Heverlee, Belgium), P. Porcher (Meudon, France) and J. C. Krupa (Orsay, France)

Absorption and emission analysis of Pr^{3+} in yttrium aluminium garnet 281
E. Antic-Fidancev, M. Lemaître-Blaise, P. Caro (Meudon, France) and J. C. Krupa (Orsay, France)

Spin-correlated crystal-field interactions in NdF_3, Nd^{3+}:LaF_3, and Nd^{3+}:$LiYF_4$ 287
C. K. Jayasankar, F. S. Richardson, M. F. Reid (Charlottesville, Va., U.S.A.), P. Porcher and P. Caro (Meudon, France)

Re-examination of the $4f^3$ energy parameters for several systems with neodymium–oxygen atom coordination 291
C. K. Jayasankar, F. S. Richardson, M. F. Reid (Charlottesville, Va., U.S.A.), P. Porcher and P. Caro (Meudon, France)

Two-photon excitation of the Sm^{2+} ion in BaClF 295
J. C. Gâcon, J. M. Marcerou and B. Jacquier (Villeurbanne, France)

Eu(III) as a sensitive probe of ligand conformation in dicyclohexyl-18-crown-6-complexes . . 297
D. Plancherel (Lausanne, Switzerland)

Importance of the ligand excess in investigations of the fluorescence intensity of the lanthanide(III) complexes of aminopolyacetic acids in aqueous solutions 299
M. Elbanowski, S. Lis, B. Makowska and J. Konarski (Poznań, Poland)

Luminescence behaviour of uranyl nitrate hydrates 301
H. D. Burrows, S. J. Formosinho and M. da Graça Miguel (Coimbra, Portugal)

Spectroscopic investigation of Eu–EDTA complexes 303
J. Dexpert-Ghys, J. Halwani and B. Piriou (Meudon, France)

Peculiar fluorescence of Eu^{3+} in oxyapatites 307
B. Piriou, D. Fahmi, J. Dexpert-Ghys (Meudon, France), A. Taitai and J. L. Lacout (Toulouse, France)

The complexation of uranyl ion with carboxylic acids studied by ^1H and ^{13}C NMR 309
M. T. Nunes (Sacavém, Portugal) and V. M. S. Gil (Coimbra, Portugal)

A NMR study of lanthanide-NOTA chelates as aqueous paramagnetic shift and relaxation probes 311
C. F. G. C. Geraldes, M. P. M. Marques (Coimbra, Portugal) and A. D. Sherry (Richardson, Tex., U.S.A.)

Lanthanum-139 NMR spectroscopy of triscyclopentadienyllanthanum(III) derivatives: a promising new tool for solution studies 315
S. H. Eggers, M. Adam, E. T. K. Haupt and R. D. Fischer (Hamburg, F. R. G.)

Anisotropy in the proton NMR paramagnetic shift of cyclooctatetraene and cyclopentadiene anions coordinated to U(IV) 319
B. R. McGarvey and S. Nagy (Windsor, Ont., Canada)

A model for describing paramagnetic Mössbauer relaxation spectra of organometallic ^{237}Np compounds 323
G. Adrian (Karlsruhe, F. R. G.)

Photoelectron spectroscopy (UPS/XPS) study of Np_2O_3 formation on the surface of neptunium metal 327
J. R. Naegele (Karlsruhe, F. R. G.), L. E. Cox and J. W. Ward (Los Alamos, N. Mex., U.S.A.)

A photoelectron study of pentavalent uranium imido complexes 331
J. B. Brennan, J. C. Green and C. M. Redfern (Oxford, U.K.)

The electronic structure of organometallic complexes of the f elements.
XIX. Parametrization of the crystal field splitting patterns of quasi trigonal bi-pyramidal anionic complexes involving the tris(η^5-cyclopentadienyl)uranium(IV) moiety 335
H.-D. Amberger, H. Reddmann (Hamburg, F.R.G.), G. Shalimoff and N. M. Edelstein (Berkeley, Calif., U.S.A.)
XXI. The crystal field splitting pattern of perdeuterated tris(η^5-cyclopentadienyl)uranium-(IV)chloride in the low energy range 339
H.-D. Amberger, H. Reddmann (Hamburg, F.R.G.) and N. M. Edelstein (Berkeley, Calif., U.S.A.)

Oscillator strengths for f → d transitions in lanthanide and actinide aqua ions 341
B. R. Judd (Baltimore, Md., U.S.A.)

Electronic Raman effect in lanthanide(III) complexes.
Ligand polarization contribution 343
J. Sztucki and W. Stręk (Wrocław, Poland)

Photostimulated oxygen exchange and photochemical properties of uranyl ions 345
S. A. Gaziev, N. G. Gorshkov, L. G. Mashirov and D. N. Suglobov (Leningrad, U.S.S.R.)

New ^{166}Er nuclear states populated in the ^{166m}Ho decay 353
Th. Ogandaga, J. Dalmasso, A. Hachem and G. Ardisson (Nice, France)

Author Index 355

Subject Index 357